

PATENT ABSTRACTS OF JAPAN

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(71)Applicant : SHIN ETSU CHEM CO LTD

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(54) PRODUCTION OF EPOXY RESIN COMPOSITION FOR SEALING SEMICONDUCTOR

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a composition well-balanced between the mold release characteristics and the flow characteristics even when highly filled with an inorganic filler in particular by heating and kneading the constituents of an epoxy resin composition in a specified order.

SOLUTION: In producing an epoxy resin composition for sealing a semiconductor by heating and kneading an epoxy resin, a curing agent, an inorganic filler a mold release agent and a cure accelerator, the epoxy resin, the curing agent and the inorganic filler are preliminarily heated and kneaded beforehand, the kneaded material is blended with the mold release agent and the cure accelerator, and the blend is further heated and kneaded. To blend the mold release agent and the cure accelerator, a method of preliminarily heating and kneading the epoxy resin the curing agent and the inorganic filler, cooling and grinding the kneaded material obtained, and blending the ground material with the mold release agent and the cure accelerator, or a method of adding the mold release agent and the cure accelerator while the epoxy resin, the curing agent and the inorganic filler are preliminarily heated and kneaded can be employed. A flexibilizer, coupling agent, flame retardant, thermoplastic resin, etc. can also be blended in any of the steps with the composition.

LEGAL STATUS

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3.1%
sph silica
3.1% 0.5-10% flex

AN 2000:631988 CAPLUS
 DN 133:223924
 ED Entered STN: 12 Sep 2000
 TI Manufacture of epoxy resin compositions for semiconductor device
 packagings
 IN Mizushima, Eisuke
 PA Shin-Etsu Chemical Industry Co., Ltd., Japan
 SO Jpn. Kokai Tokkyo Koho, 6 pp.
 CODEN: JKXXAF
 DT Patent
 LA Japanese
 IC ICM C08L063-00
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 Section cross-reference(s): 76

FAN.CNT 1

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CLASS

PATENT NO.	CLASS	PATENT FAMILY CLASSIFICATION CODES
JP 2000248158	ICM	C08L063-00
	ICS	C08K003-00; H01L023-29; H01L023-31
	IPCI	C08L0063-00 [ICM,7]; C08K0003-00 [ICS,7]; H01L0023-29 [ICS,7]; H01L0023-31 [ICS,7] <--

AB The process involves kneading epoxy resins, hardeners, and inorg. fillers, blending with mold-releasing agents and curing accelerators, and further kneading. The compns. exhibit good mold releasability and flowability. Thus a composition with spiral flow (EMMI 66) 30 in. was obtained by kneading Sumiepoxy ESCN 195 85, H 1 (phenolic resin) 50, and Fuselex RD 8 (fused SiO2) 400 parts at 90°, crushing, mixing with 15 parts WAX-E and 2 parts Curezol C 17Z (accelerator), and kneading at 90°. Its molding had Bacol hardness 60 at 175° for 60 s and mold releasability from C plate 0.5 kg/10 mm².

ST epoxy resin compn semiconductor device packaging; mold releasability epoxy resin compn packaging

IT Waxes

RL: MOA (Modifier or additive use); USES (Uses)
 (WAX-E, mold releasing agents; manufacture of epoxy resin compns. with good mold releasability and flowability for semiconductor device packagings)

IT Electronic packaging materials
 Semiconductor device fabrication

(manufacture of epoxy resin compns. with good mold releasability and flowability for semiconductor device packagings)

IT Epoxy resins, uses

RL: DEV (Device component use); IMF (Industrial manufacture); PRP (Properties); PREP (Preparation); USES (Uses)
 (novolak-crosslinked; manufacture of epoxy resin compns. with good mold releasability and flowability for semiconductor device packagings)

IT 23328-87-2, Curezol C 17Z

RL: CAT (Catalyst use); USES (Uses)
 (manufacture of epoxy resin compns. with good mold releasability and flowability for semiconductor device packagings)

IT 148821-12-9P

RL: DEV (Device component use); IMF (Industrial manufacture); PRP (Properties); PREP (Preparation); USES (Uses)
 (manufacture of epoxy resin compns. with good mold releasability and flowability for semiconductor device packagings)

IT 60676-86-0, Fuselex RD 8

RL: MOA (Modifier or additive use); USES (Uses)
 (manufacture of epoxy resin compns. with good mold releasability and flowability for semiconductor device packagings)

DERWENT-ACC-NO: 2001-010758

DERWENT-WEEK: 200108

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TITLE: Epoxy resin composition production, for sealing
semiconductors, comprises preliminarily heating and
blending epoxy resin, curing agent and inorganic filler

PATENT-ASSIGNEE: SHINETSU CHEM IND CO LTD[SHIE]

PRIORITY-DATA: 1999JP-0056718 (March 4, 1999)

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INT-CL (IPC): C08K003/00, C08L063/00 , H01L023/29 , H01L023/31

ABSTRACTED-PUB-NO: JP2000248158A

BASIC-ABSTRACT:

NOVELTY - Production of epoxy resin composition comprises preliminarily heating and blending epoxy resin, curing agent and inorganic filler and blending them together with releasing agent and curing accelerator.

USE - Sealing semiconductors in highly accumulated electronic apparatus.

ADVANTAGE - The epoxy resin composition has improved releasing property and flow property.

CHOSEN-DRAWING: Dwg.0/2

TITLE-TERMS: EPOXY RESIN COMPOSITION PRODUCE SEAL SEMICONDUCTOR COMPRISE
PRELIMINARY HEAT BLEND EPOXY RESIN CURE AGENT INORGANIC FILL

DERWENT-CLASS: A21 A85 L03 U11

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L04-C20A;

EPI-CODES: U11-E02A2;

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Polymer Index [1.2]

018 ; ND01 ; ND07 ; N9999 N6439 ; Q9999 Q7523 ; Q9999 Q7476 Q7330
; K9449 ; N9999 N6213 N6177

Polymer Index [1.3]

018 ; A999 A351 A340

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Polymer Index [1.5]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the approach of manufacturing the good epoxy resin constituent for semi-conductor closure of a mold release property and flowability.

[0002]

[Description of the Prior Art] as the manufacture approach of the epoxy resin constituent for former and semi-conductor closure -- an epoxy resin, a curing agent, and a minerals bulking agent -- and -- in addition to this -- an additive -- dry cleaning or a part -- ordinary temperature or the manufacture approach which heats, is mixed and carries out heating kneading of the blend object at once was adopted by the sentiment.

[0003] By the way, in connection with high integration of IC chip, enlargement, and the small thinning of an IC package, much more reduction in an elastic modulus and low expansion coefficient-ization are demanded in the epoxy resin constituent for semi-conductor closure. Although addition of a flexible grant agent and loading of the amount of minerals bulking agents become indispensable as the means, by the conventional manufacture approach, there is an inclination for the mold-release characteristic of the obtained semiconductor device to get remarkably bad. Although there is technique, such as the approach of changing the approach of making increase the share at the time of kneading as the technique of raising a mold-release characteristic, and raising hardenability and a hardening-accelerator kind, a hardening acceleration dose and a release agent kind, and the amount of release agents, and raising hardenability and a mold-release characteristic, in the case of the former, fluid lowering and in the case of the latter, it has the fault which causes fluid lowering and lowering of dependability.

[0004] Therefore, the object of this invention is to offer the approach of manufacturing the epoxy resin constituent for semi-conductor closure which was able to balance a mold release property and flowability, also when the fault of the above-mentioned conventional technique is abolished and high restoration of the minerals bulking agent is carried out especially at an epoxy resin constituent.

[0005]

[The means for solving a technical problem and the gestalt of implementation of invention] this invention persons came to complete this invention for the above-mentioned object being attained based on a header and this knowledge by choosing suitably the sequence of heating kneading of the component of the epoxy resin constituent for semi-conductor closure, as a result of inquiring wholeheartedly, in order to solve said technical problem.

[0006] This invention Namely, an epoxy resin, a curing agent, a minerals bulking agent, a release agent, a hardening accelerator, Furthermore, at least one sort of components chosen from a flexible grant agent, a coupling agent, a flame retarder, and thermoplastics are set if needed to the manufacture approach of the epoxy resin constituent for semi-conductor closure which carries out heating kneading. An epoxy resin, a curing agent, and a minerals bulking agent are contained, and the need is accepted further. A flexible grant agent, Preheating kneading of at least one sort of components chosen from a coupling agent, a flame retarder, and thermoplastics is carried out, and the manufacture approach of the epoxy

resin constituent for semi-conductor closure characterized by blending a release agent and a hardening accelerator with the kneading object, and carrying out heating kneading is offered.

[0007] The mold-release characteristic which is the object of release agent original falls at the same time the bonding strength of the matrix of organic resin, such as an epoxy resin and a curing agent, and minerals bulking agents, such as a silica, will decline, if the minerals bulking agent represented by a release agent and the silica when it explains in full detail per this point carries out heating kneading of both simultaneously, since compatibility is structurally high. From this, the improvement in compatibility of an organic resin matrix and a minerals bulking agent is needed as the improvement approach of a release force. Then, the compatibility of this matrix and a minerals bulking agent is raised by carrying out preheating kneading of the constituent of others which excluded the release agent beforehand, and a matrix, improvement in the bonding strength of a minerals bulking agent, and a mold-release characteristic are compatible by adding a release agent and carrying out heating kneading after that. Although there are one shaft, a biaxial extruder, etc. as this heating kneading approach, since it is easy to carry out accumulation also of any, if two heating kneading or more is performed, a fluidity will fall with that heat. Therefore, the knowledge of being necessary at the time of preheating kneading to carry out by excluding a hardening accelerator for fluid reservation is carried out.

[0008] In this invention, it is checked that the effectiveness greatest by adding a release agent and a hardening accelerator in this way at the time of the 2nd heating kneading, and carrying out heating kneading is acquired, and the effectiveness expected even if it adds other additives by the same approach at the time of the 2nd heating kneading and carries out heating kneading is not acquired.

[0009] Hereafter, lessons is taken from this invention and it explains in more detail. The epoxy resin constituent concerning this invention is manufactured using well-known additives, such as a flexible grant agent, a coupling agent, a flame retarder, and thermoplastics, an epoxy resin, a curing agent, a minerals bulking agent, a release agent, a hardening accelerator, and if needed [other].

[0010] As an epoxy resin which constitutes this epoxy resin constituent, as long as it has at least two epoxy groups in 1 molecule, you may be what kind of thing. For example, an epoxy resin with well-known bisphenol mold epoxy resins, such as novolak mold epoxy resins, such as phenol novolak mold epoxy resin and cresol novolak mold epoxy resin, bisphenol A mold epoxy resin, and bisphenol female mold epoxy resin, TORIFE Norian alkane mold epoxy resin, cycloaliphatic epoxy resin, naphthalene ring content epoxy resin, biphenyl mold epoxy resin, phenol aralkyl mold epoxy resin, biphenyl aralkyl mold epoxy resin, bicyclo pentadiene mold epoxy resin, etc. is used. Although these epoxy resins may be combined suitably, in order to carry out high restoration of the minerals bulking agent especially, a biphenyl mold epoxy resin and its naphthalene ring content epoxy resin are desirable. Softening temperature is 50-100 degrees C, and these epoxy resins have that desirable in which weight per epoxy equivalent has 100-400. Furthermore, a bromine-ized epoxy resin can be used for flameproofing.

[0011] Moreover, as a curing agent, amine compounds, such as the ingredient which stiffens this epoxy resin, for example, phenol resin, aliphatic series or aromatic series polyamine, the 2nd amine, and the 3rd amine, a carboxylic anhydride, and poly amino maleimide are used. What a thing also with these well-known curing agents is used, for example, has two or more phenolic hydroxyl groups, such as novolak resin, such as phenol novolak resin and cresol novolak resin, bisphenol mold resin, TORIFE Norian alkane mold phenol resin, naphthalene ring content phenol resin, biphenyl mold phenol resin, phenol aralkyl resin, biphenyl aralkyl mold phenol resin, bicyclo pentadiene phenol resin, and terpene ring content phenol resin, as phenol resin is mentioned. In said phenol resin, that in which softening temperature has 60-120 degrees C is desirable. As a hydroxyl equivalent, the thing of 90-150 is desirable.

[0012] The loadings of these curing agents are a hardening effective dose of the above-mentioned epoxy resin, for example, in the case of phenol resin, are usually the 25 - 100 weight section to the epoxy resin 100 weight section. Moreover, the loadings of phenol resin can also be set up so that the ratio of a mol number of the phenolic hydroxyl group in the phenol resin to the mol number of the epoxy groups in an epoxy resin may become 0.5-2.0, especially 0.8 to about 1.2.

[0013] Especially the minerals bulking agent blended with this invention makes the expansion

coefficient of a sealing agent small, when it uses as an IC package, and it reduces the stress which joins a semiconductor device. the spherical silica which can use a thing well-known also as this minerals bulking agent, for example, is manufactured with a crystalline silica and a sol-gel method as a silica filler -- one sort, such as fused silica of spherical or the letter of crushing, a fused quartz, amorphous silica, a mist silica, and a sedimentation silica, or two sorts or more can be used. Moreover, an alumina, silicon nitride, boron nitride, nitriding aluminum, a magnesia, magnesium silicate, etc. can also be used.

[0014] In addition, as occasion demands, from this, the small detailed silica of a mean diameter etc. can also be used together, and especially the mean diameter can also be mixed, although it is usual that it is [1-50-micrometer] 5-30 micrometers (as a weighted mean (or median size) for example, by a laser beam diffraction method etc.). Moreover, what carried out surface treatment beforehand by the titanium system coupling agent (for example, titanate and an organic titanium complex), the silane coupling agent (for example, organoalkoxysilane which has functionality radicals, such as an amino group, an epoxy group, a sulfhydryl group, and an alkenyl radical), etc. can be used for the above-mentioned bulking agent.

[0015] the fill of a minerals bulking agent -- the total quantity 100 weight section of a resinous principle (an epoxy resin and curing agent) -- receiving -- the 200 - 1000 weight section -- desirable -- the 280 - 900 weight section -- it is the 500 - 700 weight section more preferably. If an expansion coefficient may become large, the stress which joins a semiconductor device may increase, if the 200 weight sections are not fulfilled, a component property may deteriorate and the 1000 weight sections are exceeded, the viscosity at the time of shaping may become high, and a moldability may worsen.

[0016] In this invention, release agents other than the above-mentioned component, such as carnauba wax, a higher fatty acid, and synthetic waxes, are used. the blending ratio of coal -- the total quantity 100 weight section of an epoxy resin and a curing agent -- receiving -- 0.1 - 10 weight section -- it is 0.3 - 5 weight section preferably.

[0017] Moreover, hardening accelerators other than the above-mentioned component, such as cyclo amidine derivatives, such as phosphoretted hydrogen derivative [, such as an imidazole or its derivative, triphenylphosphine, tris p-methoxypheny phosphoretted hydrogen, and tricyclohexyl phosphoretted hydrogen], 1, and 8-diazabicyclo (5.4.0) undecene -7, are used. the blending ratio of coal -- the total quantity 100 weight section of an epoxy resin and a curing agent -- receiving -- 0.1 - 10 weight section -- it is 0.3 - 5 weight section preferably.

[0018] Furthermore, it is desirable to add the flexible grant agent of a silicone system in this invention for the reduction in stress in addition to the indispensable component mentioned above. As a flexible grant agent, the block polymer of silicone rubber powder, silicone gel, organic resin, and a silicone polymer etc. is mentioned, for example. In addition, a minerals bulking agent front face may be processed by 2 liquid type silicone rubber and silicone gel instead of adding such a flexible grant agent. Zero to 10% of the weight, if shock resistance with the desirable thing of the whole constituent considered as 1 - 5 % of the weight 0.5 to 10% of the weight and the amount used sufficient at less than 0.5 % of the weight may not be obtained and it exceeds 10 % of the weight, especially as for the amount of the above-mentioned flexible grant agent used, a mechanical strength may usually become imperfection.

[0019] Other arbitration components can be blended with the epoxy resin constituent of this invention in the range which does not bar the effectiveness of this invention if needed. As such an arbitration component, flame retarders, such as thermoplastics, such as MBS resin etc. and its hydrogenation object, a silane coupling agent, antimony oxide, and phosphorus compounds, etc. are mentioned.

[0020] It **, and in the epoxy resin constituent which consists of the above-mentioned component, beforehand, preheating kneading of an epoxy resin, a curing agent, and the minerals bulking agent is carried out, a release agent and a hardening accelerator are blended with the kneading object, and the manufacture approach of the epoxy resin constituent of this invention carries out heating kneading further, and obtains them.

[0021] It adds on the way which is carrying out preheating kneading of the approach of cooling and blending the kneading object obtained here by carrying out preheating kneading of an epoxy resin, a

curing agent, and the minerals bulking agent about the combination approach of a release agent and a hardening accelerator with what was ground or an epoxy resin, a curing agent, and the minerals bulking agent, and the approach of blending is adopted.

[0022] The former approach mixes epoxy resin A, a curing agent B, and the minerals bulking agent C with a mixer 1, as shown in drawing 1. Carry out heating kneading of this with the 1st kneading machine 2, and the grinding equipments 3, such as a crusher and a grinder, grind after cooling the obtained preliminary kneading object, and a release agent D and a hardening accelerator E are blended with this. It can mix with the mixers 4, such as the Henschel mixer, the last kneading object which kneaded this with the 2nd kneading machine 5 further, and generated it can be cooled, and the approach of pulverizing with grinding equipment 6 can be adopted.

[0023] On the other hand, as shown in drawing 2, while mixing epoxy resin A, a curing agent B, and the minerals bulking agent C with a mixer 1 and kneading this with a kneading machine 2 as the latter approach, in the way of the kneading, a release agent D and a hardening accelerator E can be blended with the quantum feeder 7 etc., kneading can be continued, and the approach of pulverizing with grinding equipment 3 can be adopted after cooling the generated last kneading object. In this case, as for combination, it is desirable to carry out among 60 - 80% preferably in that travelling direction into kneading area 2a of a kneading machine 2 after 50% in the middle of the above-mentioned release agent D and a hardening accelerator E.

[0024] As kneading machines 2 and 5 which knead [preheating-] and knead [heating-] the above-mentioned component, which thing is sufficient as 1 shaft extruder etc., and it is not restricted especially. In the case of a biaxial extruder, the said direction / different direction other side gap is sufficient also as the direction of a screw revolving shaft. Here, as for the kneading area of a kneading machine, the thing of ratio-of-length-to-diameter(screw length / diameter of screw) = 1-15, especially ratio-of-length-to-diameter = 2-10 is used suitably. Although the peripheral speed of a kneading-machine screw is selected suitably, it is good to peripheral-speed [of 5-50m] consider as a part for 10-40m/preferably by /.

[0025] In the above-mentioned kneading, it heats beyond the temperature which a part of resinous principle [at least] in a constituent fuses, and, thereby, good kneading is made. In this case, what is necessary is just to heat at about 40-120 degrees C, in order to fuse a resinous principle. In addition, the temperature of these 40-120 degrees C is whenever [stoving temperature / of a kneading machine], and by friction of the constituent kneaded etc., since it generates heat also in itself, even if the melting temperature of a constituent component is higher than whenever [this stoving temperature], at least a part may fuse it by whenever [this stoving temperature]. Moreover, as for the mixing time in each above-mentioned kneading machines 2 and 5, it is preferably good for 5 to 600 seconds that it is 10 - 240 seconds.

[0026] in addition, components, such as components other than the above, for example, a flexible grant agent, a coupling agent, a flame retarder, and thermoplastics, -- the above -- although it does not interfere even if it blends in which phase, it can usually mix and knead in the first phase with an epoxy resin, a curing agent, and a minerals bulking agent.

[0027] The obtained epoxy resin constituent can improve a mold-release characteristic, without causing fluid lowering and lowering of dependability.

[0028] The epoxy resin constituent obtained by the manufacture approach of this invention can be used for a desired application as it is, especially can be used suitable for closure of semiconductor devices, such as IC, LSI, a transistor, a thyristor, and diode, and can be used effective in manufacture of a printed circuit board etc. Here, when closing a semiconductor device, it is desirable to perform molding temperature of the epoxy resin constituent for semi-conductor closure at 150-180 degrees C, and to perform postcure at 150-180 degrees C for 2 to 16 hours.

[0029]

[Effect of the Invention] According to this invention, a mold-release characteristic can be improved by the conventional manufacture approach, without addition of the flexible grant agent which suited the inclination for the mold-release characteristic of a semiconductor device to get remarkably bad, and

loading of a minerals bulking agent causing fluid lowering and lowering of dependability in the epoxy resin constituent which becomes indispensable. Especially the manufacture approach of this invention is effective when high restoration of the minerals bulking agent is carried out (200 - 1000 weight section [as opposed to / For example, / a total of 100 weight sections of an epoxy resin and a curing agent]).

[0030]

[Example] Although an example and the example of a comparison are shown and this invention is explained concretely hereafter, this invention is not restricted to the following example. In addition, the section shows the weight section in the following example.

[0031] [An example and example of a comparison] The epoxy resin constituent of the following component was manufactured by the following approach at drawing 1 and the process which shows 2. Epoxy resin (polyglycidyl ether of o-cresol-form aldehyde novolac, Sumitomo Chemical make ESCN-195) 85 section curing agent (novolak mold phenol resin, Meiwa formation make, H-1) 50 section flexibility grant agent (dimethyl silicone oil, the Shin-Etsu Chemical make, KF-96)

10 section hardening accelerator (Shikoku formation make and imidazole C17Z) 2 section silane coupling agent () [the Shin-Etsu Chemical make,] [gamma-glycidoxo propyl TORIMETOKI] A gardenia fruit run, KBM-403 2 section release agent (the Hoechst make, a wax, WAX-E) 2 section flame retarder (the Sumitomo Metal Mining make, antimony oxide) 15 section bulking agent (fused silica, made in Tatsumori, RD-8 (mean particle diameter of 8 micrometers)) The 400 sections [0032] In manufacturing method (example 1) drawing 1, after mixing, kneading and (90 degrees C, 1 minute) grinding each component except a release agent and a hardening accelerator, the release agent and the hardening accelerator were added in this grinding object, and it mixed, kneaded and (90 degrees C, 1 minute) ground further.

[0033] (Example 2) In drawing 2, when mixing and kneading each component except a release agent and a hardening accelerator (90 degrees C, 2 minutes), the release agent and the hardening accelerator were added from the quantum feeder located to 60% to the travelling direction of kneading area, and it kneaded and ground.

[0034] (Example 1 of a comparison) In drawing 1, all components were first put in block, and it mixed, and kneaded and (90 degrees C, 1 minute) ground.

[0035] (Example 2 of a comparison) In drawing 1, after mixing, kneading and (90 degrees C, 1 minute) grinding each component except a release agent, the release agent was added in this grinding object, and it mixed, kneaded and (90 degrees C, 1 minute) ground further.

[0036] The spiral flow of the obtained epoxy resin constituent was measured, and it fabricated at 175 degrees C and the degree of hardness of 60 seconds after was measured, postcure was performed at 180 more degrees C for 5 hours, and the mold-release characteristic was measured. A result is shown in a table 1.

[0037]

[A table 1]

	実施例1	実施例2	比較例1	比較例2
スパイラルフロー (inch)	30	30	30	20
硬度 (175°C/60秒)	60	60	30	60
離型性 (kgf/10mm ²)	0.5	0.5	2.0	0.5

spiral flow: -- the approach according to EMMI-66 -- measurement degree-of-hardness: -- a bar call hardness meter -- measurement mold-release characteristic: -- Cr plate -- the shape of a circle of 10mm2 -- closing -- the measurement by part for push pull gage 60mm/

[Translation done.]

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CLAIMS

[Claim(s)]

[Claim 1] The manufacture approach of the epoxy resin constituent for semi-conductor closure which carries out preheating kneading of an epoxy resin, a curing agent, and the minerals bulking agent beforehand, and is characterized by blending a release agent and a hardening accelerator with the kneading object, and carrying out heating kneading further in the manufacture approach of the epoxy resin constituent for semi-conductor closure which consists of carrying out heating kneading of an epoxy resin, a curing agent, a minerals bulking agent, a release agent, and the hardening accelerator.

[Claim 2] The manufacture approach according to claim 1 which blends a release agent and a hardening accelerator with the grinding article which carried out preheating kneading of an epoxy resin, a curing agent, and the minerals bulking agent, and is characterized by carrying out heating kneading.

[Claim 3] The manufacture approach according to claim 1 characterized by adding a release agent and a hardening accelerator from the middle of a kneading process in case preheating kneading of an epoxy resin, a curing agent, and the minerals bulking agent is carried out.

[Claim 4] Furthermore, claim 1 characterized by blending at least one sort of components chosen from a flexible grant agent, a coupling agent, a flame retarder, and thermoplastics in one of phases thru/or the manufacture approach of three given in any 1 term.

[Translation done.]

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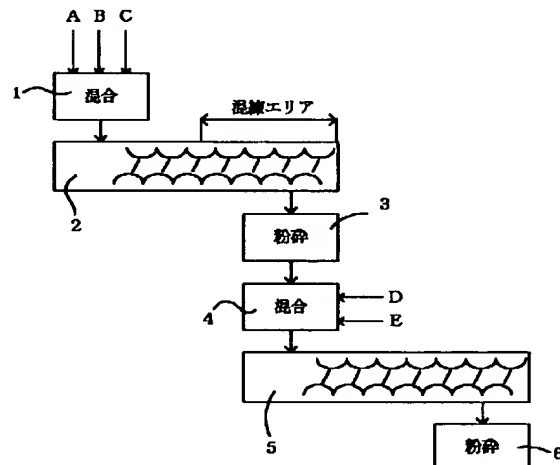
最終頁に続く

(54) 【発明の名称】 半導体封止用エポキシ樹脂組成物の製造方法

(57) 【要約】

【解決手段】 エポキシ樹脂、硬化剤、無機質充填剤、離型剤及び硬化促進剤を加熱混練することからなる半導体封止用エポキシ樹脂組成物の製造方法において、予めエポキシ樹脂、硬化剤及び無機質充填剤を予備加熱混練しておき、その混練物に離型剤と硬化促進剤とを配合して更に加熱混練することを特徴とする半導体封止用エポキシ樹脂組成物の製造方法。

【効果】 本発明によれば、従来の製造方法では半導体装置の離型性が著しく悪くなる傾向にあった可撓性付与剤の添加、無機質充填剤の増量が必要となるエポキシ樹脂組成物において、流動性の低下及び信頼性の低下を招くことなく離型性を向上できる。本発明の製造方法は、特に無機質充填剤を高充填した場合（例えば、エポキシ樹脂と硬化剤の合計100重量部に対して200～1000重量部）に有効である。



【特許請求の範囲】

【請求項1】 エポキシ樹脂、硬化剤、無機質充填剤、離型剤及び硬化促進剤を加熱混練することからなる半導体封止用エポキシ樹脂組成物の製造方法において、予めエポキシ樹脂、硬化剤及び無機質充填剤を予備加熱混練しておき、その混練物に離型剤と硬化促進剤とを配合して更に加熱混練することを特徴とする半導体封止用エポキシ樹脂組成物の製造方法。

【請求項2】 エポキシ樹脂、硬化剤及び無機質充填剤を予備加熱混練した粉砕品に離型剤と硬化促進剤を配合し、加熱混練することを特徴とする請求項1記載の製造方法。

【請求項3】 エポキシ樹脂、硬化剤及び無機質充填剤を予備加熱混練する際、離型剤と硬化促進剤を混練工程の途中から添加することを特徴とする請求項1記載の製造方法。

【請求項4】 更に、可撓性付与剤、カップリング剤、難燃剤、熱可塑性樹脂から選ばれる少なくとも1種の成分をいずれかの段階で配合することを特徴とする請求項1乃至3のいずれか1項記載の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、離型特性及び流動特性の良好な半導体封止用エポキシ樹脂組成物を製造する方法に関する。

【0002】

【従来の技術及び発明が解決しようとする課題】従来、半導体封止用エポキシ樹脂組成物の製造方法としては、エポキシ樹脂、硬化剤、無機質充填剤及びその他添加剤をドライもしくは一部ウエットで常温又は加熱して混合し、そのブレンド物を一回で加熱混練する製造方法が採用されていた。

【0003】ところで、ICチップの高集積化、大型化及びICパッケージの小型薄肉化に伴い、半導体封止用エポキシ樹脂組成物においては一層の低弾性率化、低膨張率化が要求されている。その手段としては、可撓性付与剤の添加、無機質充填剤量の増量が必須となるが、従来の製造方法では、得られた半導体装置の離型性が著しく悪くなる傾向がある。離型性を向上させる手法としては、混練時におけるシアを増加させ硬化性を上げる方法、及び硬化促進剤種、硬化促進剤量及び離型剤種、離型剤量を変更して硬化性、離型性を向上させる方法等の手法があるが、前者の場合は流動性の低下、後者の場合は流動性の低下及び信頼性の低下を招く欠点を有している。

【0004】従って、本発明の目的は、上記従来技術の欠点をなくし、特にエポキシ樹脂組成物に無機質充填剤を高充填した場合にも離型特性と流動特性のバランスのとれた半導体封止用エポキシ樹脂組成物を製造する方法を提供することにある。

【0005】

【課題を解決するための手段及び発明の実施の形態】本発明者らは、前記課題を解決するため鋭意検討を行った結果、半導体封止用エポキシ樹脂組成物の成分の加熱混練の順序を適当に選択することにより、上記目的が達成されることを見出し、この知見に基づいて本発明を完成するに至った。

【0006】即ち、本発明は、エポキシ樹脂、硬化剤、無機質充填剤、離型剤、硬化促進剤、更に必要に応じて、可撓性付与剤、カップリング剤、難燃剤及び熱可塑性樹脂から選ばれる少なくとも1種の成分を加熱混練する半導体封止用エポキシ樹脂組成物の製造方法において、エポキシ樹脂、硬化剤及び無機質充填剤を含有し、更に、必要に応じて可撓性付与剤、カップリング剤、難燃剤及び熱可塑性樹脂から選ばれる少なくとも1種の成分を予備加熱混練しておき、その混練物に離型剤と硬化促進剤とを配合して加熱混練することを特徴とする半導体封止用エポキシ樹脂組成物の製造方法を提供するものである。

【0007】この点につき詳述すると、離型剤とシリカに代表される無機質充填剤は構造的に親和性が高いため、両者を同時に加熱混練すると、エポキシ樹脂、硬化剤等の有機樹脂のマトリックスとシリカ等の無機質充填剤との結合力が低下すると同時に、離型剤本来の目的である離型性が低下する。このことより、離型力の改善方法としては、有機樹脂マトリックスと無機質充填剤の親和性向上が必要となる。そこで、予め離型剤を省いたその他の組成物を予備加熱混練することで該マトリックスと無機質充填剤の親和性を高め、その後、離型剤を加えて加熱混練することで、マトリックスと無機質充填剤の結合力の向上と離型性が両立する。この加熱混練方法としては1軸、2軸の押出機等があるが、いずれも蓄熱しやすいため、2回以上の加熱混練を行うと、その熱によって流動性が低下する。そのため、予備加熱混練時には硬化促進剤を省いて行うことが流動性確保のために必要となることを知見したものである。

【0008】本発明においては、このように離型剤と硬化促進剤を2度目の加熱混練時に添加して加熱混練することで最大の効果が得られることが確認されており、他の添加物を同様の方法で2度目の加熱混練時に添加して加熱混練しても期待する効果は得られない。

【0009】以下、本発明につき更に詳しく説明する。本発明にかかるエポキシ樹脂組成物は、エポキシ樹脂、硬化剤、無機質充填剤、離型剤、硬化促進剤、その他必要に応じて、例えば、可撓性付与剤、カップリング剤、難燃剤及び熱可塑性樹脂などの公知の添加剤を用いて製造される。

【0010】このエポキシ樹脂組成物を構成するエポキシ樹脂としては、1分子中にエポキシ基を少なくとも2個有するものであればいかなるものであってもよい。例

例えば、フェノールノボラック型エポキシ樹脂、クレゾールノボラック型エポキシ樹脂等のノボラック型エポキシ樹脂、ビスフェノールA型エポキシ樹脂、ビスフェノールF型エポキシ樹脂等のビスフェノール型エポキシ樹脂、トリフェノールアルカン型エポキシ樹脂、脂環式エポキシ樹脂、ナフタレン環含有エポキシ樹脂、ビフェニル型エポキシ樹脂、フェノールアラルキル型エポキシ樹脂、ビフェニルアラルキル型エポキシ樹脂、ビスクロペンタジエン型エポキシ樹脂などの公知のエポキシ樹脂が用いられる。これらエポキシ樹脂は、適宜組み合わせてもよいが、中でも無機質充填剤を高充填するためには、ビフェニル型エポキシ樹脂やナフタレン環含有エポキシ樹脂が望ましい。これらエポキシ樹脂は、軟化点が50～100℃で、エポキシ当量が100～400を有するものが望ましい。更に、難燃化のため、ブロム化エポキシ樹脂を使用することができる。

【0011】また、硬化剤としては、このエポキシ樹脂を硬化させる材料、例えばフェノール樹脂、脂肪族あるいは芳香族ポリアミン、第2アミン、第3アミン等のアミン化合物、カルボン酸無水物、ポリアミノマレイミド類などが用いられる。これら硬化剤も公知のものが用いられ、例えばフェノール樹脂としては、フェノールノボラック樹脂、クレゾールノボラック樹脂等のノボラック樹脂、ビスフェノール型樹脂、トリフェノールアルカン型フェノール樹脂、ナフタレン環含有フェノール樹脂、ビフェニル型フェノール樹脂、フェノールアラルキル樹脂、ビフェニルアラルキル型フェノール樹脂、ビスクロペンタジエンフェノール樹脂、テルペン環含有フェノール樹脂などのフェノール性水酸基を2個以上有するものが挙げられる。前記フェノール樹脂の中では、軟化点が60～120℃を有するものが好ましい。水酸基当量としては90～150のものが好ましい。

【0012】これらの硬化剤の配合量は、上記エポキシ樹脂の硬化有効量であり、例えばフェノール樹脂の場合、エポキシ樹脂100重量部に対し、通常25～100重量部である。また、フェノール樹脂の配合量は、エポキシ樹脂中のエポキシ基のモル数に対するフェノール樹脂中のフェノール性水酸基のモル数の比が0.5～2.0、特に0.8～1.2程度となるように設定することもできる。

【0013】本発明に配合する無機質充填剤は、特に半導体封止材として用いた場合に封止材の膨張係数を小さくし、半導体素子に加わる応力を低下させるものである。この無機質充填剤としても公知のものを使用し得、例えば、シリカフィラーとして結晶性シリカ、ゾルゲル法で製造される球状シリカ、球状又は破砕状の溶融シリカ、溶融石英、非晶質シリカ、煙霧質シリカ、沈降シリカ等の1種又は2種以上を使用することができる。また、アルミナ、窒化ケイ素、窒化ホウ素、窒化アルミ、マグネシア、マグネシウムシリケートなどを使用するこ

ともできる。

【0014】なお、その平均粒径（例えば、レーザ光回折法等による重量平均（又はメジアン径）として）は1～50μm、特に5～30μmであることが通常であるが、必要により、これより平均粒径の小さい微細シリカなどを併用、混合することもできる。また、上記充填剤は、チタン系カップリング剤（例えば、チタン酸エステルや有機チタン錯体）やシランカップリング剤（例えば、アミノ基、エポキシ基、メルカプト基、アルケニル基等の官能性基を有するオルガノアルコキシシラン）などで予め表面処理したものを使用することができる。

【0015】無機質充填剤の充填量は、樹脂成分（エポキシ樹脂及び硬化剤）の合計量100重量部に対して200～1000重量部、好ましくは280～900重量部、より好ましくは500～700重量部である。200重量部に満たないと膨張係数が大きくなって半導体素子に加わる応力が増大し、素子特性が劣化する場合があり、1000重量部を超えると成形時の粘度が高くなって成形性が悪くなる場合がある。

【0016】本発明では、上記成分の他に、カルナバワックス、高級脂肪酸、合成ワックス類などの離型剤が用いられる。その配合割合は、エポキシ樹脂及び硬化剤の合計量100重量部に対して0.1～10重量部、好ましくは0.3～5重量部である。

【0017】また、上記成分の他に、イミダゾールもしくはその誘導体、トリフェニルフォスフィン、トリスπ-メトキシフェニルフォスフィン、トリシクロヘキシルフォスフィンなどのフォスフィン誘導体、1,8-ジアザビシクロ(5.4.0)ウンデセン-7などのシクロアミジン誘導体等の硬化促進剤が用いられる。その配合割合は、エポキシ樹脂及び硬化剤の合計量100重量部に対して0.1～10重量部、好ましくは0.3～5重量部である。

【0018】更に、本発明では、上述した必須成分に加え、低応力化のためにシリコン系の可撓性付与剤を添加することが好ましい。可撓性付与剤としては、例えば、シリコンゴムパウダー、シリコンゲル、有機樹脂とシリコンポリマーとのブロックポリマーなどが挙げられる。なお、このような可撓性付与剤を添加する代わりに、二液タイプのシリコンゴムやシリコンゲルで無機質充填剤表面を処理してもよい。上記可撓性付与剤の使用量は、組成物全体の0～10重量%、通常0.5～10重量%、特に1～5重量%とすることが好ましく、使用量が0.5重量%未満では十分な耐衝撃性が得られない場合があり、10重量%を超えると機械的強度が不十分になる場合がある。

【0019】本発明のエポキシ樹脂組成物には、必要に応じてその他の任意成分を本発明の効果を妨げない範囲で配合することができる。このような任意成分としては、MBS樹脂等やその水素添加物などの熱可塑性樹

脂、シランカップリング剤、酸化アンチモン、リン化合物等の難燃剤などが挙げられる。

【0020】而して、本発明のエポキシ樹脂組成物の製造方法は、上記成分からなるエポキシ樹脂組成物において、予め、エポキシ樹脂、硬化剤及び無機質充填剤を予備加熱混練しておき、その混練物に離型剤と硬化促進剤とを配合して、更に加熱混練して得るものである。

【0021】ここで、離型剤と硬化促進剤の配合方法については、エポキシ樹脂、硬化剤及び無機質充填剤を予備加熱混練し、得られた混練物を冷却し、粉碎したものに配合する方法、あるいはエポキシ樹脂、硬化剤及び無機質充填剤を予備加熱混練している途上で添加し、配合する方法とが採用される。

【0022】前者の方法は、図1に示したように、エポキシ樹脂A、硬化剤B、無機質充填剤Cを混合機1にて混合し、これを第1混練機2にて加熱混練し、得られた予備混練物を冷却後、破砕機、粉碎機等の粉碎装置3により粉碎し、これに離型剤D、硬化促進剤Eを配合して、ヘンシェル混合機等の混合機4により混合し、これを更に第2混練機5により混練し、生成した最終混練物を冷却し、粉碎装置6により粉碎する方法を採用することができる。

【0023】一方、後者の方法としては、図2に示したように、エポキシ樹脂A、硬化剤B、無機質充填剤Cを混合機1にて混合し、これを混練機2にて混練すると共に、その混練の途上において、離型剤D、硬化促進剤Eを定量フィーダー7などにより配合し、混練を続けるもので、生成した最終混練物を冷却後、粉碎装置3により粉碎する方法を採用することができる。この場合、上記離型剤D、硬化促進剤Eの途中配合は、混練機2の混練エリア2a中において、その進行方向で50%以降、好ましくは60～80%の間に行うことが好ましい。

【0024】上記成分を予備加熱混練及び加熱混練する混練機2、5としては、1軸押出機などいずれのものでよく、特に制限されない。2軸押出機の場合、スクリュウ回転軸方向も同方向/異方向いずれでもよい。ここで、混練機の混練エリアは L/D （スクリュウ長/スクリュウ径）＝1～15、特に $L/D=2\sim10$ のものが好適に使用される。混練機スクリュウの周速は、適宜選定されるが、周速5～50m/分、好ましくは10～40m/分とするのがよい。

【0025】上記混練においては、組成物中の樹脂成分の少なくとも一部が溶融する温度以上に加熱するもの *

*で、これにより良好な混練がなされる。この場合、樹脂成分を溶融するには、40～120℃程度に加熱すればよい。なお、この40～120℃という温度は、混練機の加熱温度であり、混練される組成物の摩擦等により、それ自体でも発熱するため、組成物成分の溶融温度がこの加熱温度より高くても、この加熱温度で少なくとも一部が溶融し得る。また、上記各混練機2、5における混練時間は5～600秒、好ましくは10～240秒であることがよい。

10 【0026】なお、上記以外の成分、例えば可撓性付与剤、カップリング剤、難燃剤、熱可塑性樹脂等の成分は、上記いずれの段階で配合しても差し支えないが、通常、エポキシ樹脂、硬化剤、無機質充填剤と共に、最初の段階で混合、混練することができる。

【0027】得られたエポキシ樹脂組成物は、流動性の低下及び信頼性の低下を招くことなく、離型性を向上できるものである。

【0028】本発明の製造方法で得られたエポキシ樹脂組成物は、そのまま所望の用途に使用し得、特にIC、LSI、トランジスタ、サイリスタ、ダイオード等の半導体装置の封止用に好適に使用できるものであり、プリント回路板の製造などにも有効に使用できる。ここで、半導体装置の封止を行う場合、半導体封止用エポキシ樹脂組成物の成形温度は150～180℃、ポストキュアは150～180℃で2～16時間行うことが好ましい。

【0029】

【発明の効果】本発明によれば、従来の製造方法では半導体装置の離型性が著しく悪くなる傾向にあった可撓性付与剤の添加、無機質充填剤の増量が必要となるエポキシ樹脂組成物において、流動性の低下及び信頼性の低下を招くことなく離型性を向上できる。本発明の製造方法は、特に無機質充填剤を高充填した場合（例えば、エポキシ樹脂と硬化剤の合計100重量部に対して200～1000重量部）に有効である。

【0030】

【実施例】以下、実施例と比較例を示し、本発明を具体的に説明するが、本発明は下記の実施例に制限されるものではない。なお、下記例で部は重量部を示す。

【0031】〔実施例、比較例〕下記成分のエポキシ樹脂組成物を図1、2に示す工程で下記方法によって製造した。

エポキシ樹脂（オルソクレゾールノボラック型エポキシ樹脂、住友化学製、

ESCN-195）

85部

硬化剤（ノボラック型フェノール樹脂、明和化成製、H-1）

50部

可撓性付与剤（ジメチルシリコンオイル、信越化学工業製、KF-96）

10部

硬化促進剤（四国化成製、イミダゾールC17Z）

2部

シランカップリング剤（信越化学工業製、γ-グリシドキシプロピルトリメトキ

シシラン, KBM-403)	2部
離型剤 (ヘキスト製, ワックス, WAX-E)	2部
難燃剤 (住友金属鉱山製, 酸化アンチモン)	15部
充填剤 (溶融シリカ, 龍森製, RD-8 (平均粒径8 μ m))	400部

【0032】製造法

(実施例1) 図1において、離型剤と硬化促進剤を除く各成分を混合、混練(90℃, 1分)、粉碎した後に、この粉碎物に離型剤と硬化促進剤を添加して、更に混合、混練(90℃, 1分)、粉碎した。

【0033】(実施例2) 図2において、離型剤と硬化促進剤を除く各成分を混合、混練(90℃, 2分)する際に、混練エリアの進行方向に対して60%に位置する定量フィーダーから離型剤と硬化促進剤を添加して、混練、粉碎した。

【0034】(比較例1) 図1において、最初に全成分*

*を一括して混合し、混練(90℃, 1分)、粉碎した。

【0035】(比較例2) 図1において、離型剤を除く各成分を混合、混練(90℃, 1分)、粉碎した後に、この粉碎物に離型剤を添加して、更に混合、混練(90℃, 1分)、粉碎した。

【0036】得られたエポキシ樹脂組成物のスパイラルフローを測定し、また175℃で成形し、60秒後の硬度を測定し、更に180℃で5時間ポストキュアを行い、その離型性を測定した。結果を表1に示す。

【0037】

【表1】

	実施例1	実施例2	比較例1	比較例2
スパイラルフロー (inch)	30	30	30	20
硬度 (175℃/60秒)	60	60	30	60
離型性 (kgf/10mm ²)	0.5	0.5	2.0	0.5

スパイラルフロー: EMMI-66に準じた方法で測定

硬度: バーコール硬度計により測定

離型性: Cr板に10mm²の円状に封止し、プッシュアップ・ゲージ60mm/分での測定

【図面の簡単な説明】

【図1】本発明の第一方法を説明するフロー図である。

【図2】本発明の第二方法を説明するフロー図である。

【符号の説明】

1 混合機

2 混練機

※3 粉碎装置

4 混合機

5 混練機

6 粉碎装置

7 定量フィーダー

A エポキシ樹脂

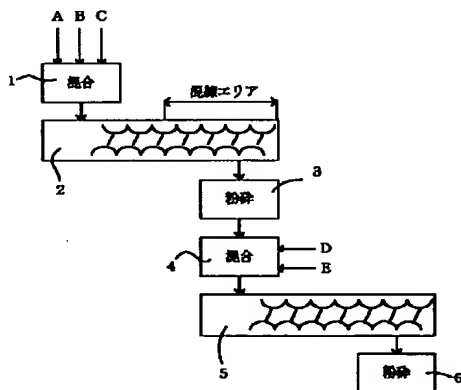
B 硬化剤

C 無機質充填剤

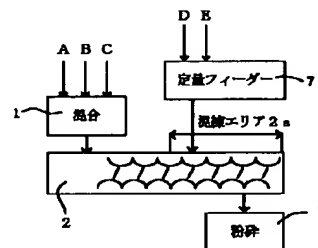
30 D 離型剤

※ E 硬化促進剤

【図1】



【図2】



フロントページの続き

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